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THE MECHANISM OF THE NITRATION OF UNSATURATED COMPOUNDS

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The nitration of olefins has been successfully studied by N. Ya. Dem'yanov [1] and his school, as well as by a number of other investigators [2, 3]. According to our ideas [4-6], the nitration of olefins, just as that of aromatic compounds, proceeds by either an ionic or radical type of reaction, depending on the conditions of the nitration [5]. In both cases, the reaction undoubtedly begins by an attack of the electrophylic nitrating agents (NO_2^+, $\cdot NO_2$, $C(NO_2)_4$, and others) on the mobile and spatially accessible π- electrons. The mobility of the π-electrons is due to the comparatively low energy of their bond with the carbon nuclei, while their accessibility is due to the peripheral arrangement of their orbits with respect to the axes of the carbon atoms. We will schematically represent these characteristics of the π-bonds by formulas of the type

$$R_2C\overset{\frown}{-}CR_2$$

The beginning stages of the nitration stated above conforms with Ostromyslenskiy's reaction, which, according to our views consists of the formation of a complex by means of penetration of π-electrons into the sphere of the electrophylic nitrogen atom, indicated in the scheme by the arrow $\longrightarrow$.

$$(NO_2)_3\text{-}C\text{-}\overset{O}{\underset{O}{\overset{\|}{N}}}\text{+}\left(\overset{CR_2}{\underset{CR_2}{|}}\right) \rightleftarrows (NO_2)_3C\text{-}\overset{O \; +\delta}{\underset{O}{\overset{\uparrow}{N}}}\leftarrow\cdots\left(\overset{CR_2}{\underset{C_2}{|}}\right) \qquad (1)$$

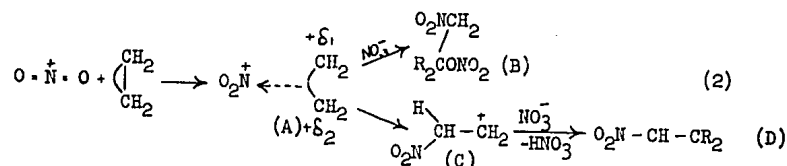$$\underbrace{}_{-2\delta} \qquad +\delta$$

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During nitration of the ionic type, as with concentrated nitric acid for example,

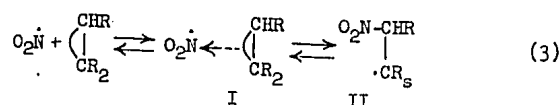$$3HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \cdot HONO_2$$

$$O \cdot \overset{+}{N} \cdot O + \Big(\overset{CH_2}{\underset{CH_2}{\big|}}\Big) \longrightarrow O_2\overset{+}{N} \leftarrow --- \Big(\overset{+\delta_1}{\underset{(A)+\delta_2}{\overset{CH_2}{\underset{CH_2}{\big|}}}} \quad \overset{NO_3^-}{\nearrow} \quad \overset{O_2NCH_2}{\underset{R_2CONO_2}{\big/}} \; (B) \qquad \overset{H}{\underset{O_2N}{\searrow}} \overset{+}{CH - CH_2} \xrightarrow[-HNO_3]{NO_3^-} O_2N - CH - CR_2 \quad (D) \qquad (2)$$

(C)
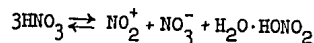
to the general theory of alkylating agents [7], can readily take on anions. For example, in the case of the reaction with NO_3^-, the complex yields the nitronitrate (B). When there is an appropriate conjugation, as, for example in the adducts of NO_2^+ to diphenylethylene or to aromatic nuclei, the complex may transform into a cation of type (C), and the latter, after giving up a proton, can transform into the substitution product (D). The orientation of the nitro group in the nitration of unsaturated and aromatic compounds can be plausibly explained by taking into account the influence of substituents on the ratio of the values δ_1 and δ_2.

Analogously, the formation of nitrosates $ON\_CH_2\_CR_2\_ONO_2$ proceeds as a rule through a preliminary formation of a complex of the olefins with the nitrating agents, particularly with the most active of them [9] -- the nitrosyl-cation NO^+ which forms during the ionization of N_2O_4 in HNO_3 [8]:

$$N_2O_4 + HNO_3 \rightleftarrows NO^+ + NO_3^- \ldots HNO_3.$$
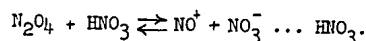
According to our ideas, the nitration of olefins with oxides of nitrogen in the absence of strong acids, takes place as a rule through the formation of complex I with the moderately electrophilic radical-like monomer of nitrogen dioxide NO_2. The complex thus formed readily converts into the free β-nitroalkyl II

$$O_2\dot{N} + \Big(\overset{CHR}{\underset{CR_2}{\big|}}\Big) \rightleftarrows O_2\dot{N} \leftarrow -- \Big(\overset{CHR}{\underset{CR_2}{\big|}} \rightleftarrows \overset{O_2N-CHR}{\underset{\cdot CR_s}{\big|}} \qquad (3)$$

I II

We computed the activation energy for the formation of the free β-nitroalkyl from the formula $E = Q + 0.13Q_\pi$ (see source 4 in bibliography), where Q denotes the heat of the reaction (3) and Q_π the energy of the π-bond. For the reaction of NO_2 with ethylene, E becomes equal to 9 kcal, for isobutylene, it is 2 kcal while for styrene, no necessity for any activation energy results, which is in accordance with direct observation.
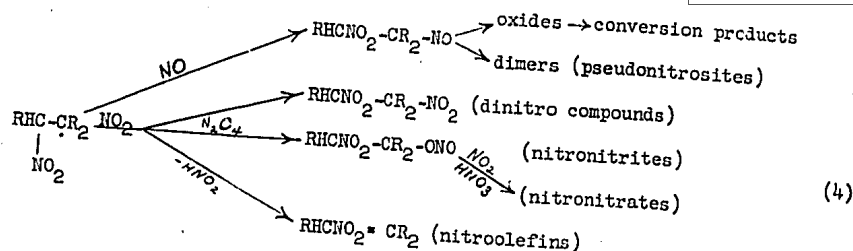
The β-nitroalkyl reacts rapidly with NO, NO_2, and N_2O_4 in a manner similar to that in the nitration of paraffins [10]:
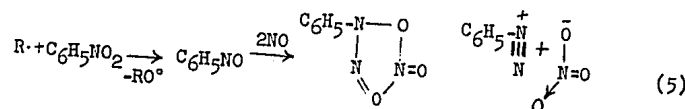
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$$RHC-CR_2 \cdot NO_2$$
$$| \quad NO_2$$

with branches:

- $\xrightarrow{NO} RHCNO_2-CR_2-NO \longrightarrow$ oxides $\rightarrow$ conversion products
  - $\searrow$ dimers (pseudonitrosites)
- $RHCNO_2-CR_2-NO_2$ (dinitro compounds)
- $\xrightarrow{N_2O_4} RHCNO_2-CR_2-ONO \xrightarrow{NO_2} \xrightarrow{HNO_3}$ (nitronitrites)
  - (nitronitrates)
- $\xrightarrow{-HNO_2} RHCNO_2 = CR_2$ (nitroolefins)

$$(4)$$

The interpretation of the mechanism of the nitration of olefins accepted here permits a reasonable interpretation of the formation of the final reaction products, at the same time indicating ways for controlling the direction of the reaction (see below). This interpretation enables us to understand the reasons why a mixture of stereoisomeric dinitrocompounds forms as a result of the action of NO_2 on stilbene or tolane /11/, why identical nitration products form from cis- and trans-isomers /12/, and finally why and in what manner nitrogen dioxide exerts a catalytic action on the transformation of these isomers (cf. equation 3).

We proved that free radicals form during the action of the oxides of nitrogen on olefins on the basis of various experimental data. An attempt to establish this comprised the chief purpose of the experimental part of our work. The proofs referred to were based on the fact that alkyls could be made to re- act with a third component which would not react with olefins otherwise.

The ability of radicals to convert aromatic nitro compounds into diazonium salts by the following scheme, which we had previously noted /4/, was used as the most convincing proof:

$$R \cdot + C_6H_5NO_2 \xrightarrow[-RO°]{} C_6H_5NO \xrightarrow{2NO}$$

$$\begin{array}{c} C_6H_5-N-O \\ | \quad | \\ N \quad N=O \\ \diagdown O \diagup \end{array} \qquad \begin{array}{c} C_6H_5-\overset{+}{N} + \overset{-}{O} \\ ||| \quad | \\ N \quad N=O \\ O \end{array} \qquad (5)$$

We were able to demonstrate the formation of noticeable quantities of phenyldiazonium nitrate (identified by the formation of a dyestuff on treat- ment with β-naphthol) by carrying out the reaction of styrene or cyclohexene with nitrogen dioxide or with dilute nitric acid in nitrobenzene being satu- rated with nitrogen oxide.

The second proof was based on the inclusion of oxygen and supplementary amounts of olefin in the reaction. At low concentrations of NO_2, this oxide of nitrogen reacts directly with the olefin when the latter is saturated with oxygen. The reaction probably proceeds according to a scheme of the type
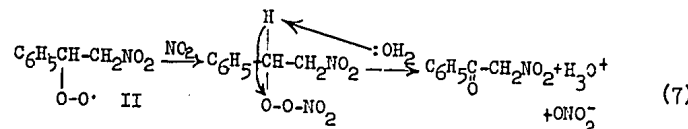
$$C_6H_5CH=CH_2 \xrightarrow{NO_2} \underset{I}{C_6H_5CH-CH_2NO_2} \xrightarrow{O_2}$$

$$\xrightarrow{} \underset{\underset{O-O \cdot \ II}{|}}{C_6H_5CH \quad CH_2NO_2} \xrightarrow{C_6H_5CH=CH_2} \underset{\underset{O-O-CH_2-CHC_6H_5}{|}}{C_6H_5CH-CH_2NO_2}, \text{ etc.} \qquad (6)$$
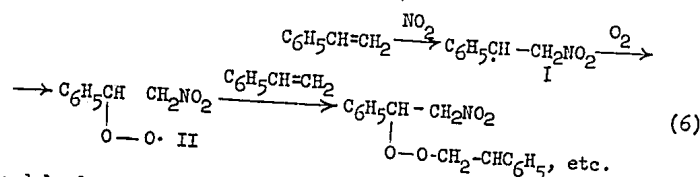
and leads to the formation of an unproportionately large amount of a viscous, high-molecular product. With a low concentration of styrene (in CCl_4), a
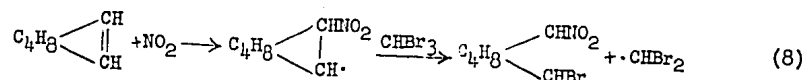
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"monomolecular" product is formed which yields ω- nitroacetophenone when treated with either water or alcohol, with a yield of 50% of theory. ω-nitroacetophenone forms mainly as a result of the following transformations:

$$C_6H_5CH-CH_2NO_2 \xrightarrow{NO_2} C_6H_5 \underset{0-0-NO_2}{\overset{H}{|}} CH-CH_2NO_2 \xrightarrow{:OH_2} C_6H_5\overset{O}{\underset{}{C}}-CH_2NO_2+H_3O^+ \qquad (7)$$
$$\underset{0-0\cdot \;\; II}{} \qquad\qquad +ONO_2^-$$

Under the conditions stated, the radical-peroxide II could rapidly add NO_2, and the ester of pernitric acid that is formed due to the strong electron- attracting action of the ONO_2 group readily gives up a proton to a proton acceptor (e.g., H_2O or C_2H_5OH). In both cases oxygen was absorbed only when the olefin reacted with NO_2; nitroacetophenone formed only when saturation with oxygen was carried out.

In the following method, the inclusion of bromoform in the reaction was achieved by carrying out the reaction with a low concentration of NO_2 and cyclohexene in the presence of the halogen compound

$$C_4H_8\underset{CH}{\overset{CH}{<}} \|\ +NO_2 \longrightarrow C_4H_8\underset{CH\cdot}{\overset{CHNO_2}{<}} | \xrightarrow{CHBr_3} C_4H_8\underset{CHBr}{\overset{CHNO_2}{<}} +\cdot CHBr_2 \qquad (8)$$

The main fraction of the product corresponded to bromonitrocyclohexane on the basis of its analysis and properties.

According to the ideas on the mechanism of the reaction represented by scheme (4), the formation of pseudonitrosite should contribute to keeping the con- centration of NO_2 low and to saturating the mass with NO. Actually when the reaction was carried out under the conditions in question in the presence of ether, the nitrosite yield was 65% of theory, which is 50% greater than Wie- land's yield /13/. A high yield of the product was also achieved by carrying out the reaction in the medium of the styrene itself; this was aided by the fact that a low concentration of NO_2 was sustained automatically.

The structure of the monomeric pseudonitrosite (nitronitroso compound) of styrene $C_6H_5CH(NO)CH_2$-NO_2 indicates that a radical mechanism is valid. If the reaction proceeded according to an ionic mechanism with an intermediate interreaction with NO^+, the formation of the nitrosite (nitrosonitrile) $C_6H_5CH(ONO)CH_2NO$ would be expected to take place. Finally, if the reaction proceeded in an ionic fashion, the nitrosoacetate $C_6H_5CH(OOC-CH_3)CH_2NO$ should have formed in acetic acid. An experiment indicated, however, that under these conditions the main product of the reaction was the pseudonitrosite, and therefore the reaction must have proceeded according to the radical type.
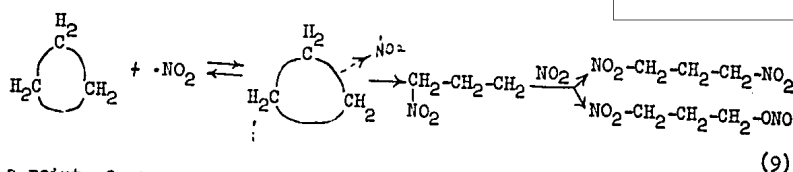
It may be assumed that the configuration of the electron orbits of the carbon atoms in cyclopropane is nearly tetrahedral. From this assumption it can be concluded that the electron orbits of the C-C bonds in cyclopropane overlap less than they normally do /in other compounds/ and that the electron density is eccentrically distributed with respect to the axis of the pair of carbon atoms involved. This leads to the conclusion that the C-C bonds in cyclopropane are similar to the usual π-bonds; this agrees with the chemical and physical properties of cyclopropane. According to this conclusion, it follows that the action of nitrating agents such as NO_2 on cyclopropane hydro- carbons takes place by a mechanism similar to the one assumed for olefins:

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$$H_2C \underset{H_2C \quad CH_2}{\overset{C_2^H}{\bigtriangleup}} + \cdot NO_2 \rightleftharpoons H_2C \underset{H_2C \quad CH_2}{\overset{C_2^{II}}{\bigtriangleup}} NO_2 \longrightarrow CH_2-CH_2-CH_2 \underset{NO_2}{\overset{NO_2}{\nearrow}} \begin{array}{l} NO_2-CH_2-CH_2-CH_2-NO_2 \\ NO_2-CH_2-CH_2-CH_2-ONO \end{array}$$

(9)

Such a point of view is confirmed by the ability of cyclopropane compounds to produce coloration with tetranitromethane (L A. Chugayev) and by the results of the nitration of tricyclene (S. S. Nametkin and A. S. Zabrodina /14/).

Following is a brief description of some of the experiments.

1. The inclusion of radicals into the reaction with nitrocompounds was accomplished by adding dropwise a solution of 4 g of NO_2 in 50 ml of a mixture of nitrobenzene and ether (4:1) to a solution of 5.2 g of styrene in 50 ml of the same mixture; the addition was carried out at 0° while agitating and passing through a stream of NO. 0.07 g of a dyestuff having a melting point of 132-133° were isolated from the reaction product after combined extraction with water and treatment of the extract with β-naphthol. After saturation for 2 hrs, with NO of a mixture of 10 g of cyclohexene, 100 ml of nitrobenzene, and 20 ml of HNO_3 of a specific gravity of 1.1, and after aqueous extraction with an alkaline solution of β-naphthol, 0.3 g of the dyestuff were obtained.

2. The inclusion of oxygen into the reaction was accomplished by first passing 2.2 liters of O_2 through a meter containing 2.6 of NO_2 at -10°, and then through 26.7 g of styrene at minus 5°. After distilling the styrene, 13.4 g of a viscous product were obtained; in a parallel experiment where CO_2 was substituted for oxygen, 6.8 g of the product were isolated. Experiments with cyclohexene yielded similar results. In order to conduct the reaction in such a manner that ω-nitroacetophenone will be formed, 2.45 g of NO_2, dissolved in 50 ml of CCl_4, were added to 3 g of styrene in 150 ml of CCl_4 over a period of 35 min at minus 5° with mechanical agitation and saturation with O_2. After distillation in vacuum at 25°, the residue, consisting of 6 g, was mixed with 30 ml of alcohol, this resulted in evolution of heat. The mixture yielded crystals of nitroacetophenone. After washing with alcohol and drying, 2.26 g of the product, melting at 105-106°, were isolated. The yield was 47% of the theoretical.

3. The inclusion of $CHBr_3$ into the reaction was accomplished as follows: A mixture of NO_2 and CO_2, prepared by passing CO_2 through a meter with one ml N_2O_4 at minus 10°, was bubbled through a solution of one gram of cyclohexene in 25 ml of $CHBr_3$ at 15°. The main fraction of the product (2.8 g), having a boiling point near 95° at 2-3 mm contained 35.4% Br.

4. In order to prepare the pseudonitrosite, a solution of 3 ml of NO_2 in 50 ml of ether previously cooled and saturated with NO was added dropwise to a mixture of 5.2 g of styrene in 50 ml of absolute ether while saturating with NO for a period of 30 min at minus 5°. The yield of the nitrosite was 5.8 g.

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